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16. ABSTRACT A 1.5 year benchmark data set was collected at biweekly frequency from two sites in shallow sand and gravel deposits in West Central Illinois. One site was near a hog-processing facility and the other represented uncontaminated conditions. Consistent sampling and analytical protocols were used to minimize errors from these sources relative to natural variability. In most cases, considerably less than 5 percent of the total variability could be attributed to sampling and analytical error. An auto-correlation analysis showed that the median sampling frequency for which the predicted ratio of effective independent sample size to total sample size was 0.5 (50 percent sampling redundancy) ranged from 6 to 14 samples per year. For a predicted ratio of effective independent sample size to total sample size of 0.9 (10 percent sampling redundancy) the sampling frequency ranged from 3 to 6 samples per year. This suggests that, for the wells sampled, sampling frequencies much higher than monthly can result in considerable loss of information, and may not be cost effective. Due to the relatively short duration of the study and effects of auto-correlation in ground-water quality constituent data, it was not possible to identify the magnitude of seasonal variations reliably. A relatively long-term data collection effort on the order of 5 to 10 years may be required for evaluation of optimal sampling frequencies for certain types of monitoring programs.

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NETWORK DESIGN FACTORS FOR ASSESSING TEMPORAL VARIABILITY IN GROUND-WATER QUALITY

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Abstract. Benchmark major ions and nutrients data were collected biweekly for about two years at 12 wells at two sites in a shallow sand and gravel aquifer in west-central Illinois. The purpose of the study was to explore the time series properties of ground-water quality data collected at a relatively high sampling frequency. A secondary purpose was to determine the relative magnitudes of natural and sampling-related sources of variance in ground-water quality time series. The absence of this kind of information has severely hindered the design of ground-water sampling programs in the past.

An autocorrelation analysis showed that the median sampling frequency for which the predicted ratio of effective independent sample size to total sample size was 0.5 (50% sampling redundancy) ranged from 6 to 14 samples per year. For a predicted ratio of effective independent sample size to total sample size of 0.9 (10% sampling redundancy) the sampling frequency ranged from 3 to 6 samples per year. This suggests that, for the wells sampled, sampling frequencies much higher than monthly can result in considerable loss of information, and may not be cost effective. Care was taken in the design of the field and laboratory sampling protocol to minimize the effects of measurement error. The data analysis confirmed that this goal was accomplished. In most cases considerably less than five percent of the total variability could be attributed to sampling and analytical error. Because of the relatively short duration of the study (42 biweekly sampling occasions at most wells) it was not possible to identify the magnitude of seasonal variations reliably.

Notice

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1. Introduction

Ground-water quality monitoring networks are designed for a number of purposes, including ambient resource studies, contaminant detection and assessment, contaminant source evaluation, litigation and research investigations. The effective design of virtually any such network depends on knowledge of the hydrogeologic system

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of interest, the presumed contaminants or water quality indicators as well as the statistical characteristics of the data being collected. Regardless of the network objectives, the interpretation of the data inevitably involves distinguishing a 'signal' from background 'noise' or natural variability.

The design of an optimal sampling network requires that the relative contributions of different sources of variability be known. In practice, of course, this is impossible. Various authors (e.g., Todd *et al.*, 1976; Sanders *et al.*, 1983; Moss *et al.*, 1978; Liggett, 1984, 1985; Gillham *et al.*, 1983) have suggested that the need for information about relative sources of variability for sampling design can be accomplished by supplementing background information with preliminary sampling results (e.g., pilot studies). In theory, this information could be used to refine the network design progressively. In many cases, however, there are insufficient background data to accomplish a reasonable initial design. So-called literature values that might be used for preliminary sampling design are virtually nonexistent, especially for the time series properties of ground-water quality that are necessary for long-term sampling design, such as is required by the Resource Conservation and Recovery Act, 1976 (RCRA) and the Comprehensive Environmental Response, Compensation, and Liability Act, 1980 (CERCLA) regulations.

Variability in the time series of ground-water chemical concentrations may arise due to 'natural' causes, physical-chemical transport properties or sampling-related variables. Examples of natural causes are inhomogenous spatial distributions of the constituents superimposed on the local and regional ground-water flow field, temporal variability in recharge, and inhomogeneities in aquifer properties (e.g., transmissivities). Physical-chemical transport properties may include dispersivities, sorptive interactions or chemical reactions. Sampling-related variables are well design, sampling devices, and field sampling and laboratory analysis protocols. Other sources of temporal variability in water-quality data which are often attributed to natural effects include hydrologic transience, the time and space variations in contaminant source, strength and composition, and the interactions between reactive chemical, biochemical and mineral constituents in recharge or flowing ground water. Our understanding of the interdependence of hydrologic, biological and chemical processes in the subsurface is limited. However, it is not necessary (or possible) to understand the relationship among these processes fully in order to design useful monitoring programs. An alternate approach, which should be adequate for sampling design purposes, is to treat most of the physical-chemical processes as black boxes, and to base the sampling design on the statistical properties (e.g., relative sources of variability) of the black boxes.

In this view, a particular set of data is regarded as simply one realization of a stochastic process, which includes both determinate (i.e., systematic) and indeterminate (i.e., random) error. Indeterminate error is the imprecision or irreproducibility of a particular observation. In statistical terms it can be characterized by the variance of the observation. Indeterminate error can be characterized by the variance of replicate determinations. Determinate error is the inaccuracy or bias between the

observed and the 'true value', if known. In practice, determinate errors can only be estimated and controlled by careful quality assurance/quality control measures. In some cases, determinate errors, or biases, which might otherwise adversely affect the decision process, can be transformed to random errors through a process of randomization in the sampling process. For instance, if it is known that a certain instrument is susceptible to 'drift' in time, then it may be advisable to randomize the sequencing of sample processing. Some determinate errors are unavoidable; for instance, disturbance of the subsurface is inevitable in ground-water quality work. Identifying and controlling these design-related errors have been the focus of much of our recent research (Barcelona *et al.*, 1983, 1985, 1986; Barcelona and Gibb, 1986).

Statistical measures of short-term temporal variability include: (1) Seasonality, which is the tendency of some variables (for instance, near-surface hydraulic heads and/or temperatures) to change systematically throughout the year; (2) Short-term trends (e.g., consequences of anthropogenic contaminant sources, spills or pumping effects); (3) Serial correlation, which, if positive, is the tendency for large observations to follow large observations and small observations to follow small observations. The reverse is true for negative correlation. However, this is virtually never seen in water quality time series. Long-term trends in data, on the other hand, are variations that occur over periods much longer than one hydrologic year (Porter and Trautmann, 1984). This categorization of temporal effects is somewhat artificial in that the combination of seasonal, short-term trends, and serial dependence may result in characteristics that cannot be differentiated quantitatively from long-term trends (see, for example, Lettenmaier and Burges, 1978). In this respect, it is important to recognize that the identification of short- or long-term trends in water quality is conditional on some knowledge of the proximity of the sampling point to the location and time of chemical release, as well as the statistical characteristics of ground-water quality variables. Water quality data which are not normally distributed pose particular challenges to statistical trend detection. A recent review by van Belle and Hughes (1984) describes some of the difficulties and recommends nonparametric tests for water quality trends.

Statistical measures of temporal variability in ground-water quality have been reviewed recently by Groeneveld and Duval (1985). In addition, Loftis *et al.* (1986), Montgomery *et al.* (1987) and Harris *et al.* (1987) cite examples of both short- and long-term temporal variability in water quality time series. Earlier reviews by Porter and Trautman (1984) and Colchin *et al.* (1978) take a statistical approach to ground-water quality assessment as well. Loftis *et al.* (1986) note in their review that few long-term observation series exist at sufficiently high sampling frequency (i.e., more frequent than quarterly) to distinguish seasonal effects from serial dependence or autocorrelation. Most water quality variables are positively skewed (nonnormal), hence commonly used parametric tests of significance to compare means or identify trends may not be appropriate (Montgomery *et al.*, 1987; Helsel and Hirsch, 1988). Transformations of variables such as logarithms are widely used to produce approximately normally distributed variates for hydrologic data.

Transformation is difficult and often unsuccessful for water quality data which may exhibit outliers (infrequent values that lie far outside the range of the data). The absence of benchmark ground-water quality observation series at high sampling frequency (i.e., monthly or biweekly) for time periods in excess of one year has made the determination of optimal sampling frequencies for ground-water quality monitoring difficult or impossible. Such data may also prove useful for the testing of statistical methods for trend analysis and for evaluation of background water quality conditions (Harris *et al.*, 1987).

The primary purposes of this study were to assess the relative contributions of variability and to identify methods to optimize sampling frequency within routine monitoring network designs. The study design controlled sampling and analytical variability to minimum values through a thorough quality assurance and quality control program. The effects of hydrologic transience were minimized in the design of the study by selection of wells drawing from water-table aquifers in both a pristine environment and at a site under the influence of a steady source of contamination. The choice of sites was expected to enable the isolation of the effect of network design variables from those due to natural or contaminant-related sources. Shallow water-table aquifers can be expected to show the greatest natural variability which enhances the ability to distinguish between natural and sampling variability. Further, many sites at which contamination problems exist affect or potentially affect shallow aquifers. This makes exploration of the statistical properties of water table aquifers especially relevant.

2. Experimental Design

2.1. Site description

Two sites were selected on the eastern flank of the Illinois River Valley in the Havana lowlands area of western Illinois. The coarse sand-and-gravel, unconfined aquifer in the region has been described previously (Walker *et al.*, 1965; Naymik and Sievers, 1983, 1985).

The uncontaminated site is located in the Sand Ridge State Forest which is in a pristine condition far removed from any sources of contamination. The area consists of a mixed hardwood and coniferous forest with prairie vegetation growing in a 20 to 30 foot (6–10 m) sequence of fine wind-blown sand. The fine dune sand overlies a 90 to 120 foot (30–40 m) sequence of coarse sand and gravel terrace material. The regional ground-water flow has a very stable directional component toward the river and is influenced by a production well field serving a state fish hatchery. Three two-inch (five cm) o.d. polytetrafluoroethylene (PTFE-Teflon®, DuPont) monitoring wells with five-foot screens were constructed at depths of 35, 50 and 65 feet (11, 15 and 21 m) by hollow-stem auger techniques in October of 1984. An additional well was completed at 105 feet (32 m) in September of 1985. The wells were all equipped with dedicated PTFE positive displacement bladder pumps (Well Wizard®,

TABLE I

Physical characteristics of the study sites and well installations

Condition of ground water	Well #	Depth		Hydraylic conductivity[Δ]		Bulk flow velocity
		Meters below land surface	Screen elevation MSL (m)	$gpd \cdot ft^{-2}$	$cm \cdot sec^{-1}$	$cm \cdot day^{-1}$
Site 1 – Sand Ridge Noncontaminated	1	11	142*	200 to 500	0.01 to 0.024	10–30
	2	15	137*	700 to 7000	0.033 to 0.33	30–50
	3	21	133*			
	4	32	120*			
Site 2 – Beardstown Contaminated	5	5.5	131	600 to 900	0.03 to 0.042	20–30
	6	7.0	129			
	8	7.5	131	500 to 800	0.02 to 0.038	40–55
	9	10	129.5			40–55
	10	10.5	128			40–55
	11**	10	129.5			40–55
	12***	10	120.5			40–55
	13	10	129.0			40–55

* Land surface 152 m above MSL (mean sea level).
** Stainless steel and *** well finished at 10 m depth along a perpendicular to the flow direction downgradient from the treatment impoundment.
Δ Modified slug test results (Hvorslev, 1951).

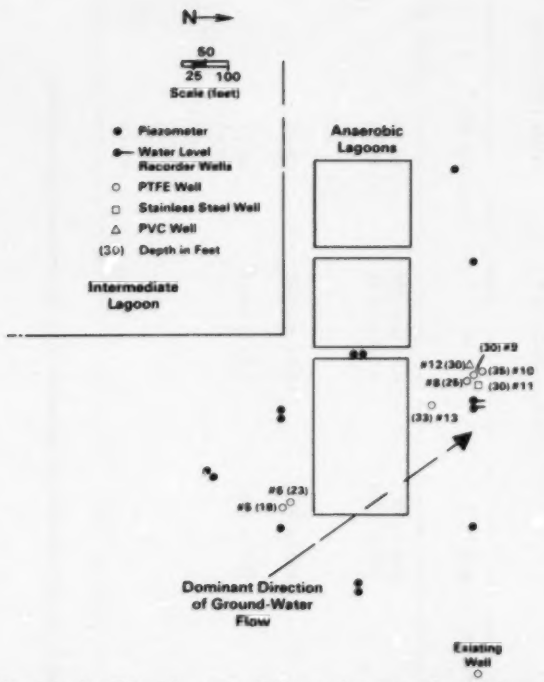

Fig. 1. Diagram of well location and relation to the contaminant source at the Beardstown site.

QED Env. Systems, Ann Arbor, MI) with PTFE air and ground-water transfer lines (Barcelona *et al.*, 1986). The monitoring well nest was supplemented by an array of shallow piezometers to monitor hydrologic conditions during the study.

The contaminated site is located on an industrial property in Beardstown, Illinois. The site is in the southern lobe of the shallow unconfined aquifer in the Havana lowlands adjacent to an anaerobic treatment impoundment for meat processing wastes. After a preliminary hydrogeochemical survey, PTFE sampling wells were constructed similarly to those at Site 1 at locations upgradient and downgradient from the impoundments during October of 1985. The upgradient nest, consisting of 18 ft. (5.5 m) and 23 ft. (~7.0 m), two-inch (five-cm) o.d. PTFE monitoring wells with five-foot screens, was located about 50 ft. (16 m) upgradient from the impoundment. Downgradient wells were located ~50 ft (16 m) from the impoundment at a depth of 33 ft. (10 m) and in a nest approximately 200 ft. (~60 m) further downgradient at depths of 25, 30 and 35 feet (7.5, 9 and 10.5 m). The installation at Beardstown was also supplemented with a number of piezometers for water level measurements. The physical characteristics of the two sites are summarized in Table I with the general condition of ground-water quality denoted in the left margin. The four nested wells (i.e., wells 1, 2, 3 and 4) in the Sand Ridge State Forest provide a vertical sequence to observe water quality variability with depth in a pristine

TABLE II

Chemical constituents of interest in ground-water monitoring

Type of analyte	Analyte	Laboratory/Field determination L or F	Information applications				
			Water quality	Drinking H_2O suitability	Contamination indicators	Possible source impacts	Geochemical evaluation of data
Geochemical	pH, Eh	F	X	X	X	X	X
	Conductivity						
	Temperature						
	Dissolved oxygen		X				X
	Alkalinity	F (Field Filtered, FF)			X	X	X
	Ca^{++}, Mg^{++}	L (Field Filtered, FF)					X
	Na^{+}, K^{+}	L (Field Filtered, FF)	X	X			
	Cl^{-}, $SO_4^{=}$, $PO_4^{=}$	F (Field Filtered, FF)	X	X	X	X	X
	Silicate	L (Field Filtered, FF)					X
Water Quality	Trace Metals						
	(Fe, Mn	L					
	Cr, Cd	(FF)	X	X	X	X	X
	Pb, Cu)						
	NO_3^{-}, NH_4^{+}	L(FF)	X	X	X	X	X
	F^{-}	L(FF)	X	X		X	
	TOC	L	X	X	X	X	
	TOX		X	X	X	X	
	TDS	L					
		(FF)	X	X	X	X	X
	Organic Compounds	L	X	X	X	X	

environment. The other sampling points include upgradient (i.e., wells 5 and 6) and downgradient wells (i.e., wells 13, 8, 9, 10, 11, 12) along the general ground-water flow path beneath the anaerobic impoundment at the contaminated site. The latter two groups of wells are illustrated in plan view in Figure 1 which also shows the location of the piezometers for water level measurements.

2.2. Sampling

From March 1986 through the fall of 1987, sampling was conducted on a biweekly basis at both sites for the range of major ionic, water quality, and geochemical parameters shown in Table II. These parameters were supplemented by determinations of methane, ferrous iron and sulfide to provide additional geochemical information as well as for the other potential network design purposes noted in the table. Water level measurements were made in all sampling wells in addition to the numerous piezometers at each site on each sampling date. The wells were purged at rates of 1 to 1.5 liter·min^{-1}, removing an average of ~5 well volumes until purging indicator parameters stabilized prior to sampling. Stabilization was noted when the pH, Eh and conductivity values changed less than 0.05 pH units, ±10 mv or ±10 μS·cm^{-1}, respectively over successive well volumes (Garske and Schock, 1986). Samples for volatile organic compounds, TOC, and TOX were collected at a flow rate of ~100 mL·min^{-1}, while other samples were collected at flow rates of ~1 L·min^{-1}. In-line filtration (0.4 μm Nucleopore®), relying on pump pressure, was used for samples collected for determinations of trace metal and dissolved inorganic species. The samples contacted only PTFE tubing and stainless steel (fittings and filtration apparatus) prior to collection and preservation in appropriate vessels. Measurements of the purging parameters (i.e., pH, Eh, and conductivity) as well as temperature, total alkalinity, Winkler-titration and electrometric-probe dissolved oxygen determinations, were made according to methods described previously (Barcelona *et al.*, 1985). Sampling operations were conducted from a specially outfitted sampling van equipped with a generator, refrigerator, air compressor for bladder pump drive gas, and adequate bench space for maintaining the integrity of the water samples and conducting preservation or analytical procedures. Appropriate field blanks, standards and duplicate samples were included for each day of sampling to insure data quality control. At least one sample from each site on each sampling date was selected at random for processing as a duplicate.

2.3. Analysis

Analytical procedures approved by the USEPA (1980) were used for most of the ionic, water quality and geochemical parameters. Total dissolved metals were determined by the single-solution modification of the USEPA atomic absorption spectrophotometry procedure developed by Smith *et al.* (1983). Sulfate determinations in the contaminated water samples from the downgradient Beardstown wells were done by potentiometric titration with $Pb(NO_3)_2$ after cation exchange, $La(NO_3)_3$ addition to remove phosphate, and adjustment of ionic strength and pH. Analytical determi-

nations were performed in duplicate for all parameters except for methane, sulfide and the field electrometric determinations of pH, dissolved oxygen and temperature. Eh values were recorded with two platinum $-$Ag/AgCl reference combination electrodes calibrated each day and at each site relative to Zobell's solution (1946) at the temperature of measurement.

3. Results and Discussion

3.1. Water quality composition

It is useful to have an appreciation for the composition of the ground-water at the two sites. Average chemical constituent concentrations for samples from selected wells over the sampling period of the wells are shown in Table III. With the exception of sodium, chloride, pH and alkalinity the major ionic composition of the ground-water samples was similar. Comparison of the results for wells #1 and #4 (i.e., the shallowest and deepest wells, respectively, at the uncontaminated site) showed the difference between fully oxidized and suboxic subsurface redox conditions (Barcelona *et al.*, 1989). There was a very strong gradient of oxygen concentration and redox potential with depth in this unconfined sand and gravel aquifer, and the average concentrations of ferrous iron mirror these changes. A chemical gradient in calcium carbonate solubility from oversaturation towards equilibrium with increased depth was also evident. These chemical gradients as well as the hydrologic gradient and flow direction were very stable during the study, although regional water levels have dropped at a rate of $\sim$1.2 ft (0.37 m) per year over this period. The steady rate of water level decline has been observed since 1982 due to the well-field operations of the fish hatchery downgradient from Site 1.

The results for the ground-water samples from the contaminated site clearly showed the marked difference one would expect between locations upgradient and downgradient from a leaking anaerobic treatment impoundment. The influent to the treatment impoundment may be characterized as an organic-rich aqueous waste stream with $\sim$0.1% dry volatile solids content. The effluent from the impoundments reflects the products of anaerobic degradation processes, since it contains high levels of alkalinity, methane, ammonia, total organic carbon and nonvolatile dissolved solids. Ground-water flow rate and direction did not vary significantly from that shown in Figure 1 during the study period. Dissolved oxygen levels at both locations at the contaminated site (Table III) were consistently at or near the detection limit for oxygen electrode measurements and below the corresponding limit for iodometric titration by the Winkler method. Ground-water quality conditions were markedly changed at downgradient locations by the leakage of leachate from the anaerobic impoundment. The downgradient ground-water samples were generally much higher in the major components of the impoundment effluent; dissolved solids, total organic carbon, methane, alkalinity, ammonia, sulfide, iron, chloride, sodium and potassium than were samples from upgradient positions. Time-series plots for the

TABLE III

Average results for ground-water chemical analyses**

Well # / Parameter (units)	1	4		5		8			
		Mean	S.D.	Mean	S.D.	Mean	S.D.	Mean	S.D.
Eh* (mv)		456	91	110	50	226	33	102	27
Ω^{-1}* ($\mu S \cdot cm^{-1}$)		359	11	225	11	375	97	1607	173
pH*		7.75	0.53	7.80	0.37	6.48	0.35	6.87	0.20
T* (°C)		12.0	0.9	12.2	0.3	12.5	2.7	15.6	1.6
TOC		0.85	0.26	0.57	0.2	3.08	0.75	6.78	1.17
TOX ($\mu g \cdot L^{-1}$)		3.65	5.0	3.07	4.0	6.26	4.6	10.9	7.6
CH_4		−0.12Δ	0.8	0.01	0.08	0.00	0.036	1.33	0.71
$NO_2^- - N$		0.00	0.002	0.00	0.001	0.00	0.002	0.01	0.004
NH_3		−0.01	0.014	0.06	0.04	0.26	0.15	174	51.3
Fe (II)		0.01	0.04	0.50	0.08	1.04	0.18	2.21	0.82
Fe_T (T = total)		0.01	0.03	0.44	0.10	1.02	0.23	2.15	0.78
Mn_T		0.00	0.009	0.15	0.03	0.09	0.02	0.63	0.10
$S^=$		0.00	0.03	0.00	0.005	0.04	0.01	0.14	0.07
O_2 (probe)*		9.00	0.50	0.61	0.27	0.36	0.13	0.36	0.18
O_2 (Winkler)*		8.82	0.86	0.46	0.06	N.D.	N.D.	N.D	N.D.
Alkalinity* (as $CaCO_3$)		216	12	132	5.4	65.5	5.7	690	81
Cl^-		2.19	0.71	1.67	0.72	66.6	38.9	141	10.1
$(NO_3^- + NO_2^-) - N$		0.95	0.2	−0.01	0.07	−0.02	0.023	1.89	2.07
$SO_4^=$		36.2	5.8	22.1	4.49	76.7	13.1	35.6	5.59
o-$PO_4^=$		0.02	0.02	0.11	0.023	0.06	0.03	14.6	7.7
T-$PO_4^=$		0.04	0.074	0.13	0.05	0.10	0.05	14.7	7.6
Silica		15.5	0.4	15.7	0.62	13.3	1.08	19.0	4.95
Ca^{2+}		65.9	3.3	38.4	2.36	38.5	8.6	44.1	7.1
Mg^{2+}		22.6	1.25	12.3	0.62	14.7	3.1	17.5	2.2
Na^{2+}		3.11	0.49	3.53	0.54	33.9	11.9	117	14.6
K^+		0.71	0.08	0.73	0.09	2.85	0.82	22.7	2.47
Depth		35′ (11 m)		105′ (32 m)		upgradient 18′ (5.5 m)		downgradient 25′ (7.5 m)	

S.D. Standard Deviation in concentration or similar units.
N.D. Not Detected.
* Determined in the field.
** Values represent the results in $mg \cdot L^{-1}$, unless otherwise specified for duplicate determinations on each of 39 sampling dates over the study period.
Δ Negative mean values result from the reporting of actual sample results above and below the limit of detection as recommended by ASTM, 1987.

five preliminary and thirty-nine sequential biweekly runs are shown in Figure 2 for well-head temperature, total organic carbon, ferrous iron and sulfide for wells #1 through #4 at the Sand Ridge site. Corresponding plots for the wells along the flow path at the contaminated site are shown in Figure 3. There were no obvious temporal trends for these constituents at the pristine Sand Ridge site (Figure 2).

The well-head temperature measurements (Figure 3a) for the upgradient wells (i.e., #5 and #6) at the contaminated site, however, show evidence of periodic variability. The trends were not directly related to known periods of recharge. The same relative hydraulic head differences between wells 6, 13 and 10 were maintained throughout the study. The temperatures from the downgradient wells did not show periodic variability presumably due to the 5 to 8 °C temperature increase downgradient which was a consequence of high microbial activity in the leachate-impacted ground water. The remaining portions of Figure 3 contain similar time series for a major component of the leachate, TOC (3b) and indicators of geochemical conditions, ferrous iron (3c) and sulfide (3d) for the wells at the contaminated site. The ferrous iron series for well #6 upgradient reflects some periodic variability which precedes the apparent maxima in temperature noted in 3a. It should be noted that the major specific constituents in the contaminated ground water are inorganic species and contaminant indicators or surrogates like TOC. Levels of volatile halocarbons or other purgeable contaminants were observed to be below 1 $\mu g \cdot L^{-1}$ and these determinations were stopped early in the study period.

The major waste constituents observed at the contaminated site are common components of landfill leachates (Zenone *et al.*, 1975; USEPA, 1977) coal gasification wastes (Humenick and Mattox, 1988), sewage and septic waste ponds or disposal operations (USEPA, 1977; Kehew *et al.*, 1983), and bear some similarity to the soluble constituents of livestock feedlot waste streams (USEPA, 1977). The results of the present study therefore have relevance to many subsurface hydrogeochemical situations.

3.2. Data quality

During the course of the study more than 55 000 analytical determinations were made on blanks, standards and samples. The final dataset was 96% complete, that is, a recovery of 96% of the maximum possible number of samples and subsequent analytical determinations were successfully completed. Outliers were screened successively at ± 3 and ± 2 standard deviations from the mean levels. In most cases, this screening revealed apparent errors in calculations, calibration or data entry which were corrected prior to data analysis. For all wells and constituents, the maximum number of samples which were identified as possible outliers and for which no documented error was identified was four percent of the total. No adjustment was made to apparent outliers for which no documented error could be identified. It should be noted that very few ($< 5\%$) of the chemical constituent results for any of the wells showed any clear tendency towards normality judging from the results of the Shapiro-Wilk W statistic test (1965).

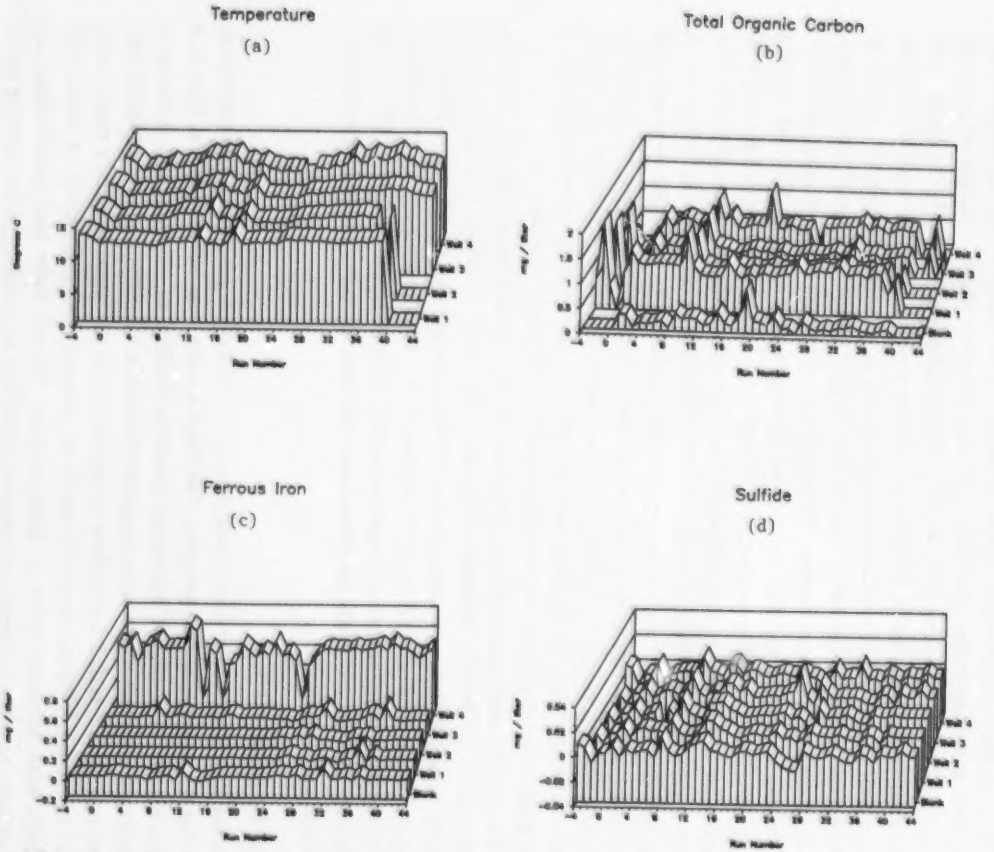

Fig. 2. Time series of flow cell temperature (2a), total organic carbon (2b), ferrous iron (2c), and suifide (2d) for the wells at the Sand Ridge site.

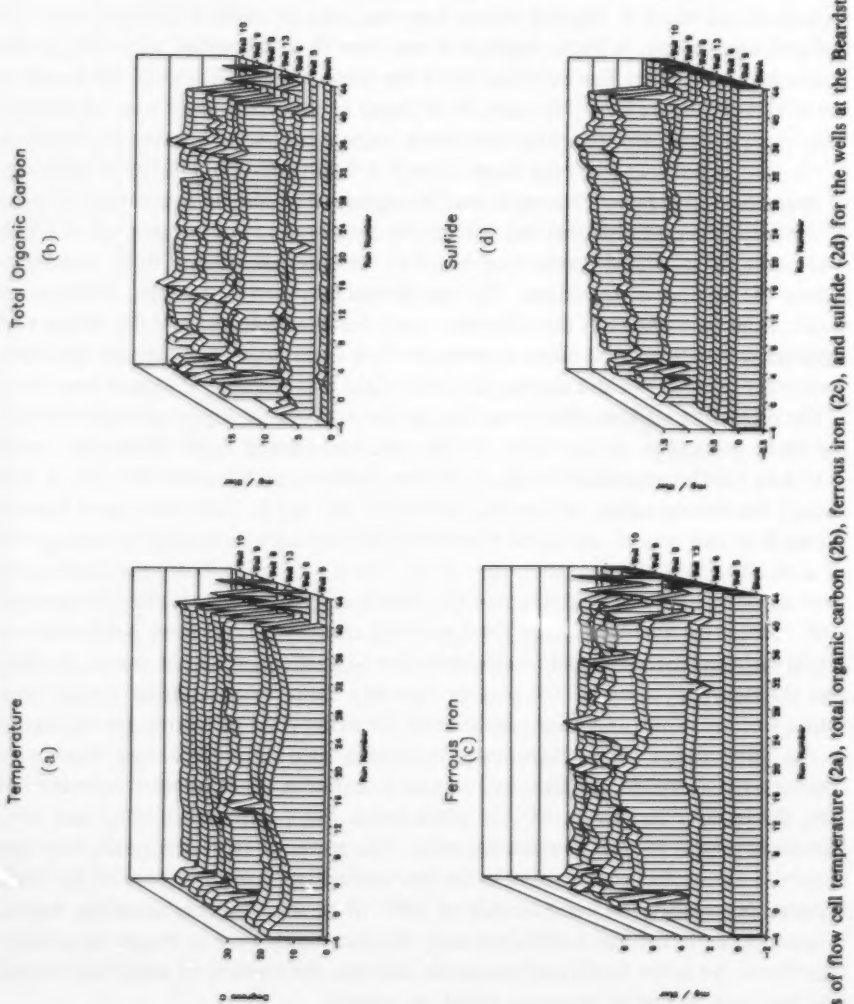

Fig. 3. Time series of flow cell temperature (2a), total organic carbon (2b), ferrous iron (2c), and sulfide (2d) for the wells at the Beardstown site.

Analyses were performed on the Quality Assurance/Quality Control data to determine if there was evidence of temporal variability in the blanks and standards or field standard recoveries and to determine if there was a concentration-related dependence in the accuracy or precision of these datasets. A time series was constructed for the field and laboratory QA/QC samples (i.e., field and laboratory standards and blanks). Missing values were removed to create a complete series of reduced sample size. A linear regression was then fit to the series, with time as the independent variable. The significance of the slope (time coefficient) was tested at the 0.05 significance level. No cases were found in which the slope was significant. This result in itself was somewhat surprising, since the expected number of rejections of the null hypothesis (that the slope is zero) is 0.05 times the number of analyses, or approximately seven. This result may be explained by the discrete nature of some of the data (especially blanks) and perhaps by nonnormality or outliers, all of which may make the true significance level less than the nominal value of 0.05, and hence reduce the number of rejections. The test should be powerful enough, however, to detect large time trends in the laboratory and field procedures, and the absence of significant trends may be taken as evidence that there was no significant temporal variability in the blank and standards which might bias the sample dataset over time.

The procedure outlined above was also applied to the sample percent recovery data for three groupings of the wells: (1) the uncontaminated Sand Ridge site (wells #1–#4), (2) the upgradient wells at the Beardstown contaminated site (#5 & #6) and (3) the downgradient wells at this site (wells #8–#13). Time series were formed for each of two sets of analytical determinations for each chemical for each group of wells. The first reflects laboratory error only (i.e., two replicate determinations were made on samples spiked within the laboratory) while the second incorporates both laboratory and field error (two replicate determinations were performed on actual samples). Separate time series also were constructed from the mean, median, and standard deviation of the percent recovery data. No significant trends were found for any of the chemical constituents for either field or laboratory recoveries in the Sand Ridge wells. Significant increasing recovery trends with time were observed for the mean, median, and standard deviation of the percent recoveries of NH_3 (laboratory and field), $SO_4^=$ (field only), Fe^{2+} (laboratory only) and Mn_T (laboratory only) for the Beardstown wells. The apparent recovery trends were due largely to difficulties encountered in the five preliminary sampling runs of the study between November 1985 and March of 1986 when the biweekly sampling began. When these early samples were eliminated, the time trends were no longer statistically significant. As in the blank and standards analysis, the number of significant trends was less than would be expected based on chance.

The average overall sampling and analytical accuracy and precision values for the chemical constituents are shown in Table IV. The levels of overall accuracy and precision routinely achieved during the project were routinely within acceptable limits for the laboratory analytical methods (USEPA, 1980). Exceptions to this level of performance were noted for constituents which were consistently present at or near

TABLE IV

Average overall accuracy and precision for the chemical constituents determined in the study

Param.	Overall		Sand Ridge		Beardstown	
	Acc.	Prec.	Acc.	Prec.	Acc.	Prec.
NH_3	95.90	23.49	91.99	29.80	100.09	12.54
$T\text{-}PO_4$	99.64	8.60	100.95	9.28	98.24	7.56
Fe^{+2}	96.07	18.80	NA*	NA	96.07	18.80
NO_2^-	82.17	36.29	81.07	35.00	83.27	37.50
$S^=$	NA	NA	NA	NA	NA	NA
NO_3^-	100.35	10.27	98.85	7.82	101.97	12.17
SiO_2	99.47	5.03	100.21	2.97	98.71	6.41
$o\text{-}PO_4$	103.44	15.38	106.54	20.77	100.12	2.32
Cl^-	105.78	32.59	112.01	46.55	100.18	1.52
SO_4^-	95.77	21.85	94.73	6.58	97.24	33.07
Ca	98.36	3.88	98.65	3.76	98.07	3.98
Mg	99.15	8.70	99.90	10.72	98.42	6.03
Na	101.69	12.17	103.51	16.16	99.95	5.87
K	97.85	5.17	99.10	5.15	96.63	4.89
Fe	99.22	5.80	100.34	7.20	98.04	3.46
Mn	101.04	6.46	101.28	8.17	100.79	3.92

* NA indicates that the number of observations for which accuracy and precision could be determined was less than five, principally due to a larger number of below detection limit results.

analytical detection limits (e.g., Cl^-, Fe(II), $S^=$). The QA/QC data analyses demonstrate that the sampling and analytical protocols employed in the study were in control.

3.3. Estimation of sources of variation

In order to insure that monitoring resources are optimally allocated, it is important to identify the sources of natural (i.e., spatial and temporal) and sampling and analytical variance.

The general statistical approach to reducing the effect of any source of variation is to randomize and collect replicates. Therefore, the effects of natural variability can only be reduced by increasing the sample size (that is, either the sampling frequency or the length of the data collection series). Increasing the sample size has the effect of reducing the component of the variance of, for instance, the long-term mean attributable to field and lab errors as well. In addition, if the component of the total variance due to laboratory and/or field errors is large, it can be reduced by taking more than one field or laboratory replicate at each sampling occasion. Whether or not collection of laboratory or field replicates is cost effective depends on the fraction of the total variance attributable to each source. The conceptual model used to estimate sources of variation was:

$$\sigma_t^2 = \sigma_n^2 + \sigma_f^2 + \sigma_l^2$$

where

σ_t^2 = total variance
σ_n^2 = natural variance
σ_l^2 = laboratory analytical
σ_f^2 = field sampling variance

Generally, the natural variations in water quality time series are of interest. For instance, the difference between the time series of a given contaminant at a downgradient and an upgradient well may give an indication of whether contaminant release has occurred. However, the difference series is inevitably corrupted by errors in the field data collection and laboratory analysis procedures, both of which introduce what may be considered 'noise' into the time series. Each of these noise processes has a variance, and the total variance is the sum of the three variance terms. This model assumes that the three sources of variation are statistically independent, which is a reasonable assumption because the sources are physically independent. A possible exception is that the magnitude of the field and laboratory errors may depend on the true value of the chemical concentration. This consideration is addressed below.

The sources of variation were estimated as follows. First, the laboratory analytical variance was estimated by taking the difference of the laboratory calibration standards series, since each standard was subjected to two replicate analytical determinations. Each difference was normalized by dividing it by the (known) true value of the standard. Then, a normalized standard deviation was computed using the inner-quartile differences (i.e., 75th minus 25th percentiles) multiplied by an adjustment factor appropriate to the normal distribution. The use of the adjustment factor for the normal distribution does not imply that the distributions were in fact normal (most were not), it is only a convenience. Next, a similar procedure was applied to the field replicate series. Because the field replicates include the effect of laboratory analytical variability as well, the analysis of the field replicates provided estimates of the sum of the normalized laboratory and field sampling variance. The normalized field sampling variance was then estimated by subtraction. This subtraction occasionally gave negative values, which were reported as 'NA'. An alternative procedure would be to simply set these values (i.e., the normalized field variance) to zero. Finally, the normalized total variance was estimated from the entire time series at each well, and for each chemical constituent where the normalization was by the median for the given well. The normalized natural variance was then estimated by subtraction.

The results are summarized in Table V for the three groups of wells. For almost all of the groups, and for almost all of the chemical constituents, a high fraction of the total variation was natural. This is consistent with the QA/QC data analyses, which showed that the data collection errors were generally quite small. The entries in the table have been separated into water quality parameters and chemical parameters of geochemical interest. The results confirm that if careful sampling and

analytical protocols are used, the natural variability in the major ion chemistry of the system can be identified. For TOC and TOX it is clear that 'natural' sources of variability are greater than the combined lab and field variance. However, the level of overall variability in TOX results was quite large in comparison to the mean values for each well. The significance of these determinations at the microgram per liter level is doubtful.

A similar attempt to estimate sources of variations in ground-water quality data was performed by Summers *et al.* (1985). They analyzed data from two sources on related ground-water samples collected in the vicinity of power plant waste disposal impoundments. They reported that, in general, combined sampling and analytical variability was less than the natural variability. Summers *et al.* (1985) noted that

TABLE V

Percentage of variance attributable to laboratory error, field error, and natural variability by chemical and site

Type of parameter	Sand Ridge			Beardstown (upgradient)			Beardstown (downgradient)		
	lab	field	nat	lab	field	nat	lab	field	nat
Water quality									
NO_3^-	0.0	00.0	100.0	0.1	NA*	99.9	0.2	NA	99.8
$SO_4^=$	0.0	0.0	100.0	0.2	NA	99.8	1.4	0.1	98.6
SiO_2	0.0	NA	100.0	0.0	20.0	80.0	0.0	6.8	93.2
$o\text{-}PO_4^=$	1.2	1.2	97.6	0.0	0.0	100.0	0.0	0.0	100.0
$T\text{-}PO_4^=$	0.0	NA	100.0	2.8	NA	97.8	0.9	NA	99.1
Cl^-	7.2	NA	92.8	0.0	3.3	96.7	0.0	17.2	82.8
Ca	0.0	45.7	54.3	0.0	2.3	97.7	0.0	3.6	96.4
Mg	0.0	20.0	80.0	0.0	2.2	97.8	0.0	2.8	97.2
Na	0.0	NA	100.0	0.0	0.3	99.7	0.0	7.1	92.9
K	0.0	NA	100.0	33.9	NA	66.1	87.1	NA	12.9
Geochmical									
NH_3	0.0	0.0	100.0	0.0	0.0	100.0	0.0	0.0	100.0
NO_2^-	NA	NA	NA	0.1	NA	99.9	0.3	NA	99.7
$S^=$	NA	NA	NA	NA	NA	NA	NA	NA	NA
Fe^{+2}	NA	NA	NA	0.0	0.1	99.9	0.0	5.9	94.1
Fe_T	0.0	NA	100.0	0.0	0.0	100.0	0.0	NA	100.0
Mn_T	0.0	NA	100.0	0.0	40.1	59.9	0.0	73.6	26.4
Contaminant indicator	lab + field**			lab + field			lab + field		
TOC	15.4		84.6	29.9		70.1	40.6		59.5
TOX	0.0		100.0	12.5		87.5	24.6		75.4

* NA indicated that the number of observations on which the estimated variance was based was less than 5, or the estimated variance was negative.

** True field spiked standards no available for these constituents demanding combined estimates of laboratory and field variability.

combined sampling and analytical variability was usually less than ~15% of the total variability which is consistent with the results of the present study. They did, however, report exceptions in the cases of NO_3^-, silicate and Zn where the combined sampling and analytical variance exceeded 30% of the total variance. The potential sensitivity of these constituents to well construction and sampling errors was not discussed in their report.

The implication of the results of this study and that of Summers *et al.* (1985) is that network design optimization efforts should focus primarily on the natural variability. The use of field and laboratory replication for purposes other than QA/QC will be difficult to justify as long as the sampling and analytical protocols are in control. This conclusion must be qualified, however. The chemical constituents present at appreciable concentrations (i.e., $mg \cdot L^{-1}$) at either site are the major cations and anions and general water quality indicators. The analytical and sampling variances for trace organic contaminants would be expected to be higher and their analytical recoveries are frequently found to be a function of concentration. In this case the field and laboratory variations may not be independent, which would violate a basic assumption in this model. Nonetheless, particular care should be given to establishing acceptable performance levels for the accuracy and precision of field and laboratory operations. The field and analytical data were collected with very careful QA/QC in the course of this research project. It is unlikely that combinations of different laboratories and field sampling crews would be able to achieve and maintain such low levels of error. Further, the sites were picked specifically to provide stable hydrologic conditions of ground-water flow and direction as well as a steadily leaking source of contamination. The effect of these conditions would be to minimize natural variability which makes the degree of sampling and analytical control all the more critical.

3.4. Temporal variations in ground-water quality

There are numerous examples of both short- and long-term variability in ground-water quality in the literature. Recent reviews by Loftis *et al.* (1986) and Montgomery *et al.* (1987) pointed out the need for very careful selection of statistical methods and for qualified interpretations of existing datasets. The well-documented cases of both short- and long-term temporal variability in ground-water quality have been tabulated in Tables VI and VII, respectively. These observations cover temporal variability caused by agricultural and nonagricultural sources in high-volume water supply production wells, observation, monitoring, and shallow private wells from a variety of hydrogeologic settings. The concentration variations are noted mainly as multiples above and below an arbitrary baseline or background concentration. In a few instances, where the trends were clearly very long-term or cyclic (i.e., due to alternate pumping and nonpumping conditions), the variations have been entered in concentration units.

Although the details of purging, sampling, filtration/preservation, and analysis were frequently lacking in the reports, very substantial variability has been docu-

TABLE VI

Observations of temporal variations in ground-water quality: short-term variations

	Constituents (concentration variation)	Nature of variability		Reference
		Period	Probable cause	
Agricultural sources	Se (± 2 mg·L^{-1})	Monthly	Irrigation/return/indeterminate	Crist (1974)*
	NO_3^- (1-3X) $SO_4^=$ (3-7X)	Minutes	Pumpage/head changes and leaching from unsaturates zone	Schmidt (1977)*
	$NO_3^=$ (1-4X)	Minutes	Pumpage/vertical stratification	Eccles *et al.* (1977)*
	NO_3^- (1-10X) $SO_4^=$ (1-1.5X)	Monthly	Irrigation/fertilizer applications/ leaching; locational differences apparent	Spalding and Exner (1980)
	NO_3^- (0.5-2X) Atrazine (1-5X)	Hours to weeks	Surface runoff recharge	Libra *et al.* (1986)
Non-Agricultural or mixed sources	H_2S (1-5X) $SO_4^=$ (1-1.2X) NH_3 (1-3X)	Minutes to hours	Pumping rate and well drilling	Colchin *et al.* (1978)*
	NO_3^- (1-13X) $SO_4^=$ (1-2X)	Minutes to hours	Pumping rate and purging	Humenick *et al.* (1980)*
	Fe (1-3X) Mn (1-1.5X)	Minutes	Purging	Wilson and Rouse (1983)
	PCE, TCE, 1,2-t-DCE (1-10X)	Minutes	Pumping rate and purging	Keely and Wolf (1983)*
	TCE (2-10X) Fe^{2+} (1-110X) $S^=$ (1-15X)	Monthly to weekly	Pumping rate and development of cone of depression	McReynolds (1986)*
	Volatile halocarbons (1-8X)	Minutes	Purging	Barcelona and Helfrich (1986)

* Denotes variations observed in water supply production wells, PCE = perchloroethylene, TCE = trichloroethylene, 1,2-t-DCE = 1,2 trans-dichloroethylene.

TABLE VII

Observations of temporal variations in ground-water quality: long-term variations

	Constituents (concentration variation)	Nature of variability		Reference
		Period	Probable cause	
Agricultural sources	Cl^- (+1.5X) $SO_4^=$ (2-4X)	Decades	Irrigation/recharge	Evenson (1965)*
	NO_3^- (3-6X) $SO_4^=$ (3-7X)	Seasonal	Irrigation/precipitation	Tenorio *et al.* (1969)*
	NO_3^- (± 48 mg·L^{-1} yr^{-1})	Seasonal	Leaching/recharge	Tryon (1976)
	NO_3^- (1-12X) $SO_4^=$ (1-1.5X)	Seasonal	Irrigation/fertilizer applications	Spalding and Exner (1980)
	NO_3^- (1-5X)	Seasonal	Recharge/fertilizer applications	Rajagopal and Talcott (1983)
	NO_3^- (1-1.5X) Pesticides (1-1.5X)	Years-seasonal	Infiltration/recharge	Libra *et al.* (1986)
Non-Agricultural or mixed sources	Conductance (2-3X) $SO_4^=$ (1-3.5X) Hardness (2-6X)	Seasonal	H_2O level fluctuations freezing/thawing recharge	Feulner and Shupp (1963)
	Conductance (+2,000 μS·cm^{-1})	Decades	Irrigation/upconing of saline water	Handy *et al.* (1969)*
	NO_3^- (± 55 mg·L^{-1} yr^{-1})	Seasonal	Sewage/fertilizer recharge and applications	Perlmutter and Koch (1972)
	Cl^- (1-3X)	Seasonal	Oil field brine/recharge	Pettyjohn (1976), (1982)
	PCE ($\pm$1-20X)	Seasonal	Infiltrated surface water quality variations	Schwarzenbach *et al.* (1983)
	TCE ($\pm$1-3X)	Seasonal	Pumping rate and patterns in well field	McReynolds (1986)*

* Denotes variations observed in water supply production wells, PCE = perchloroethylene, TCE = trichloroethlylene.

mented over time-frames ranging from minutes to decades. Significant short-term temporal concentration variability has been observed in low yield wells (i.e., monitoring and observation wells) largely resulting from purging effects (Wilson and Rouse, 1983; Barcelona and Helfrich, 1986). Similar variations of one to ten times the initial or background concentrations have been noted in samples from high-volume production wells due to pumping rate, initial pumping after periods of inactivity or due to cone of depression development (Schmidt, 1977; Eccles *et al.*, 1977; Colchin *et al.*, 1978; Keely and Wolf, 1983; McReynolds, 1986). The magnitude of short-term concentration variations noted in the literature strongly suggests that the analysis of ambient resource water quality datasets must be undertaken with careful attention to the pumping procedures used in purging and sample collection. This observation is particularly critical in relatively sparse datasets where annual 'mean' concentrations may be determined from programs with low sampling frequency (i.e., less frequently than quarterly).

Similar cautions in interpretations of long-term datasets apply in the analysis of trends at varying or unequal sampling frequencies due to the relatively short duration of the records in comparison to the length of apparent annual to multi-year variations. It was expected that the high sampling frequency (i.e., biweekly) and consistent purging and sampling procedures employed in this study would permit the identification of optimal frequencies for monitoring water quality variations under stable hydrologic and contaminant source conditions. For this reason, field sampling and laboratory analytical protocols were carefully controlled.

3.5. Sampling Frequency

The primary purpose of the project was to investigate the optimal sampling frequency for ground-water quality monitoring. Strictly speaking, there is no required or minimum sampling frequency. However, there is a relationship between the information content of the data and the sampling frequency. The term 'information' is sometimes used loosely, but in a statistical context, it can be given a more precise definition, depending on the use of the data. The most common definition of information (e.g., in the Fisher sense) is in terms of the variance of the mean, $\mathrm{Var}(\bar{x}) = \sigma^2/n$, where $\bar{x}$ is the sample mean, n is the sample size, and σ^2 is the variance of the data (Matalas and Langbein (1962)). The reciprocal of the variance of the mean is a measure of the information content of the data. If the σ^2 is large, or the sample size small, the information content is low. While this definition of information applies to estimation of the mean, the power of trend detection (in space or time) is related to the variance of the mean as well.

As noted in the previous section, the total variance is made up of the natural variance and the variance attributable to the sample collection process (field sampling and laboratory error). Most monitoring programs are intended to discriminate some effect (e.g., the long-term mean in the case of baseline sampling, or the difference in the mean between upgradient and downgradient wells in the case of RCRA sampling) from the total variation in the time series. The effect of sample collection

variance might be reduced by replicate sampling. Although, the sample collection variance made up such a small fraction of the total variance that this probably would not be worthwhile for data similar to that described here. The effect of natural variation can only be reduced by increasing the number of samples (increased sampling frequency or length of sample collection). Increasing the number of samples also reduces the effect of the sampling variance. Seemingly, the information content of the data could be increased arbitrarily, since it depends linearly on the sample size. In practice, though, the data are correlated in time (autocorrelated), and the autocorrelation increases with the sampling frequency. When the data are autocorrelated, the variance of the mean can be reexpressed as $\mathrm{Var}(\bar{x}) = \sigma^2/n_{ef}$, where n_{ef} is an effective independent sample size, which depends on the autocorrelation (Bayley and Hammersley, 1946). The value of n_{ef} is always less than n, the actual sample size, if the autocorrelation is positive, as it usually is in practice. If the model that describes the autocorrelation is the lag-one Markov process, n_{ef} approaches an upper limit as the sampling frequency increases, regardless of how large n becomes (Lettenmaier, 1976). Lettenmaier found that the lag-one process provided a reasonable description of many water quality time series. It is often difficult to extend the analysis of water quality data beyond lag-one because the autocorrelation function becomes excessively noisy.

The ratio n_{ef}/n can be considered to be a measure of the loss of information due to autocorrelation in the data. Although n_{ef} always increases with n for positive autocorrelation, n_{ef} may increase quite slowly if the autocorrelation is high. For this reason, one of the analyses conducted was to estimate a model of the serial dependence (i.e., autocorrelation) in the observed chemical series. The procedure used was as follows: First, all missing values were removed, to form a series with no missing values. This procedure is straightforward, but has the disadvantage that the interval between observations is not constant (i.e., is greater than two weeks) when there are missing observations. The effect of this approach, as compared to a much more laborious procedure that would concurrently estimate the missing data and the time series model (e.g., Lettenmaier, 1980) is to bias the autocorrelation estimates down slightly. The practical effect is minimal so long as the number of missing observations is small, which was usually the case for the chemical constituents determined in this study.

Second, an outlier screening test was applied, as described in Section 3.2. Finally, a lag one autoregressive (lag one Markov) model was fit to the data. Diagnostic procedures described in Box and Jenkins (1970) were applied to check the model fit. Specifically, the diagnostic checks used were Portmanteau's test and Anderson's test applied to the estimated model residuals. The number of cases in which the diagnostic tests were failed was only slightly larger than would be expected by chance. In most of those cases that failed the diagnostic test, there was apparent strong seasonality in the data, as described below. In all cases, the estimated lag one correlation was retained, and averaged with the other estimates for the same chemical in the given well group.

Seasonality and long-term trends in the data presented a major complication in the analysis. There are well-structured methods for handling seasonality in time series, but none are applicable to the relatively short (i.e., in terms of total duration) chemical time series that were available for analysis. The problem is that, to properly estimate a seasonal model, a relatively large number of seasonal cycles (e.g., at least 10) are required; this corresponds to, say, ten years of data, which greatly exceeds the length of the sampling horizon. Ignoring the seasonality tends to inflate the estimate of the autocorrelation coefficient, as does the existence of trends in the data. There is no completely satisfactory solution to this problem. Our approach was to identify series with apparent strong seasonality or long-term trends subjectively.

TABLE VIII

Subjective estimate of strength of seasonality or trend in variables by location

	Sand Ridge (1-4)	Beardstown (upgradient)	Beardstown (downgradient)	Number of violations
pH				0
Cond	•	+	+	2
Temp C	+	+	+	6
Temp W	+	+	+	4
Eh				1
Probe O_2				0
Wink O_2				0
Alk	•	+	•	1
NH_3				3
NO_3 N				1
NO_3NO_2 N				0
HS^-			•	0
SO_4		•	•	0
SiO_2		•		0
o-PO_4			•	1
T-PO_4			•	1
Cl^-		•	+	2
Fe^2			•	3
Ca	•	•	+	1
Mg	•	•		2
Na		•	•	3
K		•	•	3
Fe_T				0
Mn_T		•	+	0
TOX				2
VOC				6
NVOC			•	4
TOC			•	3

+ Indicates strongly seasonal.

• Indicates apparent trend or possible seasonality.

TOC = VOC + NVOC; Total Organic Carbon = Volatile Organic Carbon + Nonvolatile Organic Carbon.

(Seasonality in some variables, such as temperature, is apparent, and can be argued from first principles.) Table VIII identifies those series for which there was apparent strong seasonality, as well as the number of violations of the diagnostic checks for each variable and well group. The maximum possible number of violations for each variable was twice the number of wells in the group, since two tests were applied. Subsequent results for series showing a high number of rejections, or for which there was strong apparent seasonality or long-term trends, should be interpreted with caution. However, these problems were not an issue for a large number of series. By summarizing the results over well groups, and to a more limited extent, over chemical constituents, it is possible to give a general picture of the sampling frequency dependence of the effective independent sample size, which is relatively unaffected by the peculiarities of individual variables or sites.

Table IX gives the average lag one correlation for each variable and well group, ordered by the sum of the ranks over all well groups. Variables at the top of the list

TABLE IX

Ranking of average lag one correlation over all sites, from smallest to largest

	Sand Ridge (1-4)	Beardstown (5-6)	Beardstown (8-13)	Summed rank	Average (over all three well groups) (rho)
NO_2^- N	0.27	0.42	0.37	17	0.35
Fe_2^+	0.01	0.86	0.56	18	0.48
pH	0.51	0.47	0.20	25	0.39
$S^=$	0.16	0.36	0.67	26	0.40
NH_3	0.29	0.82	0.26	28	0.46
SiO_2	0.37	0.76	0.24	28	0.46
Mn_T	0.51	0.47	0.20	28	0.39
Probe O_2	0.41	0.66	0.44	30	0.51
T-$PO_4^=$	0.06	0.20	0.86	32	0.37
O-$PO_4^=$	0.10	0.19	0.91	33	0.40
Eh	0.46	0.60	0.60	34	0.55
$NO_3NO_2^-$N	0.75	0.35	0.42	36	0.51
TOC	0.46	0.60	0.60	37	0.55
$SO_4^=$	0.59	0.53	0.52	39	0.55
Fe_T	0.21	0.90	0.66	40	0.59
K	0.31	0.89	0.71	46	0.64
Ca	0.45	0.92	0.66	50	0.68
Mg	0.49	0.91	0.65	50	0.68
Cl^-	0.19	0.96	0.75	54	0.63
Na	0.47	0.95	0.65	56	0.69
Alk	0.73	0.69	0.76	62	0.73
Ion balance	0.73	0.92	0.79	69	0.75
Temp C	0.54	0.92	0.79	69	0.75
VOC	0.54	0.92	0.79	70	0.75
Cond	0.80	0.94	0.75	73	0.83
TOX	0.80	0.94	0.75	74	0.83
Temp W	0.66	0.97	0.78	76	0.80
NVOC	0.66	0.97	0.78	77	0.80

tended to have the lowest autocorrelation, while variables at the bottom were most highly autocorrelated. Also given is the average autocorrelation over all three well groups. Autocorrelations tended to be stronger at the Beardstown wells than at Sand Ridge, and were higher at the Beardstown upgradient wells than at the downgradient wells. The latter effect may be due to randomness introduced by the release, migration and transformation of the contaminants. It is of interest that the autocorrelations for almost all variables, even those with no apparent trends or seasonality, were quite high, suggesting that there was considerable redundancy in the data at a biweekly sampling frequency.

To illustrate the effect of the autocorrelation on sampling frequency, we solved for the sampling interval, in weeks, that would result in ratios $n_{ef}/n = 0.5$, 0.8, and 0.9 using Equation 13 of Lettenmaier (1976). Alternatively, these can be interpreted as relative losses of information due to autocorrelation in the data of 50, 20, and 10%. The results are given in Table X. At Sand Ridge, the implied loss of information is about 50% for many variables at a weekly sampling frequency, 20 percent for many variables at sampling intervals in the range of 4–8 weeks, and 10% for the majority of variables at a sampling interval of 8 weeks of more. At the Beardstown wells, the loss of information at high sampling frequencies was much greater. At the upgradient wells, which had the highest autocorrelation, the inferred loss of information of 50% occurred for several variables at a sampling interval of over 26 weeks. Information loss of between 20 and 10% was inferred for some variables at sampling intervals exceeding one year. This effect is particularly evident for Na^+, Cl^- and well temperature (TEMPW) which showed a consistent increasing trend over the study period.

The results of the study indicate that, for the major chemical constituents (i.e., water quality or contaminant indicator), quarterly sampling represents a good starting point for a preliminary network design. This frequency, of course, must be evaluated with respect to the purpose and time-frame over which the network will be conducted. Under the conditions of this study, sampling four to six times per year would provide an estimated information loss below 20% and minimize redundancy. The results for reactive, geochemical constituents suggest that bimonthly sampling frequency would be a good starting point if chemical reactivity and transformation are of concern.

Caution must be exercised in interpretation of the results due to the effects of seasonality and long-term trends. However, it should be clear that there is considerable redundancy in the data at the two-week sampling interval used, and that, at similar sites and for most of the variables studied, operational sampling programs would be inefficient at sampling frequencies in excess of bimonthly. The practical implication of this is that, for many operational monitoring programs, a relatively long time horizon (e.g. on the order of ten years) may be required to obtain adequate information for decision-making purposes, given that high frequency sampling will not yield much increase in information. It is important to emphasize that the information from sampling depends on the effective independent sample size, not

TABLE X

Sampling intervals in weeks for given ratio of effective to independent sample size, based on the estimated lag one markov model

	n_{ef}/n		
	0.5	0.8	.9
Sand Ridge			
NO_2^- N	2	4	5
Fe^{2+}	1	1	2
pH	4	7	9
S^-	2	3	4
NH_3	2	4	5
SiO_2	3	5	6
Mn_T	4	7	9
Probe O_2	3	5	7
T-$PO_4^{=}$	1	2	3
O-$PO_4^{=}$	1	2	3
Eh	3	6	8
$NO_3NO_2^-N$	8	16	21
TOC	3	6	8
$SO_4^{=}$	5	9	12
Fe_T	2	3	4
K	2	4	5
Ca	3	6	8
Mg	4	7	9
Cl^-	2	3	4
Na	3	6	8
Alk	7	14	19
Ion balance	7	14	19
Temp C	4	8	10
VOC	4	8	10
Cond	10	20	27
TOX	10	20	27
Temp W	6	11	15
NVOC	6	11	15
Beardstown upgradient			
NO_2^- N	3	6	7
Fe^{2+}	15	29	39
pH	3	6	8
S^-	3	5	6
NH_3	11	22	30
SiO_2	8	16	22
Mn_T	3	6	8
Probe O_2	6	11	15
T-$PO_4^{=}$	2	3	4
O-$PO_4^{=}$	2	3	4
Eh	5	9	12
$NO_3NO_2^-N$	3	5	6
TOC	5	9	12
$SO_4^{=}$	4	7	10
Fe_T	21	42	56

TABLE X

(Continued)

	n_{ef}/n		
	0.5	0.8	.9
K	19	38	51
Ca	26	53	71
Mg	23	47	62
Cl^-	53	107	144
Na	42	85	114
Alk	6	12	16
Ion balance	6	12	16
Temp C	26	53	71
VOC	26	53	71
Cond	35	71	95
TOX	35	71	95
Temp W	71	143	192
NVOC	71	143	192
Beardstown downgradient			
NO_2^- N	3	5	6
Fe^{2+}	4	8	11
pH	2	3	4
S^-	6	11	15
NH_3	2	4	5
SiO_2	2	4	5
Mn_T	2	3	4
Probe O_2	3	6	8
T-$PO_4^=$	15	29	39
O-$PO_4^=$	23	47	62
Eh	5	9	12
$NO_3NO_2^-N$	3	6	7
TOC	5	9	12
$SO_4^=$	4	7	9
Fe_T	6	11	15
K	7	13	18
Ca	6	11	15
Mg	5	11	14
Cl^-	8	16	21
Na	5	11	14
Alk	8	16	22
Ion balance	8	16	22
Temp C	10	19	25
VOC	10	19	25
Cond	8	16	21
TOX	8	16	21
Temp W	9	18	24
NVOC	9	18	24

just the ratio n_{ef}/n. Therefore, if the autocorrelation is large so that a relatively low sampling frequency is necessary to avoid sampling redundancy, the total length of the sampling period must be increased to achieve sufficient information return. Our results cannot simply be interpreted to mean, for instance, that quarterly sampling is adequate, unless that interpretation is couched in terms of the time horizon of the sampling program.

4. Conclusions

For the data analyzed, the fraction of the total variance attributable to sampling error was less than 10% for almost all constituents. These low sampling variance fractions are attributable to consistent, detailed protocols for sampling and analysis employed in connection with a strict QA/QC program. The sampling variance fractions achieved in this study are probably near the lower limit of what can be expected in practice. For trace organic compound determinations, the sampling variance fractions would likely be much higher. For the relatively low sampling variance fractions indicated, field and laboratory replication would likely not be cost effective, except as required for the QA/QC program.

Apparent levels of temporal variability in ground-water quality noted in the literature are very sensitive to pumping rate and duration during well purging and sample collection operations. These effects may be large compared to long-term temporal variability attributable to 'natural' causes. Purging and pumping effects on ground-water chemical results must be better understood and controlled to properly focus on natural or contaminant source-related variability.

In agreement with the results of previous studies, distributions of all ground-water quality variables were most often nonnormal (positively skewed). In addition, most constituents were strongly autocorrelated at the biweekly sampling frequency. Because of the relatively short length of the data collection program, it was difficult to quantify seasonality or time-trends even under stable hydrologic and steady contaminant source release conditions. The potential implications for the design of source detection and contamination assessment monitoring systems may be serious. Sampling at high frequencies for background conditions may entail considerable loss of information due to redundancy. Depending on monitoring objectives, much longer sampling periods may be required than are common at this time to achieve adequate information for decision-making. A relatively long time data collection horizon of the order of five to ten years may be necessary for temporally variable constituents since high sampling frequencies may not yield significant increases in information.

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